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6	Remarkable interfacial dielectric relaxation of physically cross-linked ice-hydrogel
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31 Abstract

32 In the conventional scenario, it is believed that a hydrogel consists of polymer structural 33 network filled with water droplets, a typical two-phase coexisting structure, while the 34 polymer-water interfacial layer might not be a substantial component in determining the 35 structure and functionality. Unfortunately, it is challenging to unveil the properties of the 36 interfacial layer if any, owing to the multiple phase nature and structural complexity of 37 hydrogel. In this work, the morphology and microstructures of the well-known non-covalent 38 bonding dominant polyacrylonitrile (PAN)-based hydrogels are characterized, confirming that 39 the as-prepared hydrogels do consist of polymer-network and filled water droplets. The 40 dielectric relaxation behaviors in the ice-hydrogel state with different water/ice content are 41 investigated in details by means of dielectric relaxation spectroscopy (DRS), in order to avoid 42 the electrode polarization (EP) effect non-negligible in liquid-hydrogels particularly in the 43 low-frequency range. The DRS data demonstrate the remarkable dielectric response 44 contributed from the polymer-ice interfacial layer which likely accommodates a high density 45 of polar molecules / dipoles. The temperature-dependent dielectric relaxation behaviors of the 46 ice-hydrogels with different water contents are discussed, and the thermal-activation energy for the interfacial polar structure may be likely extracted from the dielectric loss peak data. It 47 48 is found that this energy is roughly consistent with the typical bonding energy of non-covalent 49 bonding dominant hydrogels. This study represents a substantial step towards understanding 50 the interfacial coupling in hydrogels, an issue less touched so far.

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52 Keywords: Ice-hydrogels, dielectric relaxation, polar molecules, interfacial layer

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55 INTRODUCTION

Hydrogels represent a class of soft and wet materials consisting of three-dimensional (3D) cross-linked networks that can hold a high content of water, and the most known hydrogel is jelly ^[1]. While the chemical and/or physical cross-linking of polymer chains maintain the structural integrity of hydrogels, many hydrophilic groups such as -NH₂, -COOH, -OH, -OH, -CONH₂, -CONH-, and -SO₃H can be introduced so that a large amount of water can be

absorbed into these networks, as measured by 53.3% - 95.6% water occupation in volume ^[2-5]. 61 62 Due to this specific microstructure and chemical bonding nature, hydrogels possess many unique properties such as stimuli-responsiveness, shock absorption, low sliding friction, 63 flexibility, and among others ^[6], and thus great potentials in environmental engineering, 64 flexible electronics, and biomaterials ^[7-11]. While hydrogels contain water phase and polymer 65 phase, their inter-connected composite constitutes the network-like gels. Usually the polymer 66 phase can be categorized into two classes, one is polymers dominant with covalent-bonding 67 68 and the other is those dominant with non-covalent-bonding. The corresponding hydrogels are 69 called the covalently bonded hydrogels or non-covalently bonded ones. Most hydrogels are 70 more or less mechanically weak and brittle, due to the non-homogeneous cross-linking and dominant covalent bonding ^[2,6]. On this condition, it is urgent to design hydrogels with 71 72 favorable properties such as enhanced strength, toughness, processability, and dynamic adaptability^[12-14]. One approach is to introduce more non-covalent bonds^[15]. Those polymer 73 chains with non-covalent bonding, including hydrophobic interaction, H-bonding, ionic / 74 75 electrostatic interactions, and van der Waals interactions, are widely introduced, allowing not 76 only excellent mechanical properties but also sensitive response to various environmental stimuli ^[5,12,16-19]. Consequently, these hydrogels may be called smart hydrogels with balanced 77 mechanical properties, rapid responses, and intelligent functionalities among others ^[11,19]. 78

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80 In fact, various non-covalently bonded hydrogels have been synthesized. For examples, 81 Vlassak *et al* designed a hybrid hydrogel network, in which the crystalline polymer (PVA) 82 phase maintains the structural stability and reversibility, and the covalently cross-linked hydrophilic polymer (PAAm) phase maintains the network elasticity ^[20]. The polyacrylonitrile 83 84 (PAN)-based hydrogels represent one class of hybrid hydrogels receiving attention recently. 85 Liu et al reported the identification of various non-covalent bonds in PAN-based hydrogels, 86 and the dipole-dipole interaction contributes to the high mechanical strength with excellent fatigue resistance ^[21]. Similar strategy can be extended toward multiple non-covalent bonding, 87 such as dual physical coupling that combines the dipole-dipole pairing and H-bonding into the 88 hydrogel networks ^[4,22]. Nowadays it becomes a universal way to improve the hydrogel 89

90 performance by such strategy, and the non-covalent interactions are the essential ingredients
91 to achieve high stability and reversibility ^[12,23].

92

93 In order to understand the underlying mechanism for these functionalities, advanced 94 characterization become an issue of concern. Structurally, for 3D hydrophilic polymeric 95 network, the filled water phase may be viewed as a composite of free water phase which can flow freely and bound water phase which is confined in the polymer-water interfacial layer. 96 97 Therefore, the dynamic behavior of the bond-coupling inside the interfacial layer should be 98 comprehensively understood. Nevertheless, so far this property seems to be less touched than 99 the two bulk phases themselves. One may take PAN-based hydrogel as object for discussion. 100 The dominant non-covalent bonding in PAN-based hydrogels includes the dipole-dipole coupling and H-bonding, respectively corresponding to the CN-CN dipole pairs and 101 AAm-AAm H-bonds, is schematically shown in Figure 1 for a guide of eyes ^[4]. Those 102 103 hydrophilic groups -NH₂, -CONH₂, and -SO₃H, associated with the polymeric chains, may 104 also establish their non-covalent bonding with water molecules, thus allowing high-density of 105 interfacial polar units, as labelled with blue arrows in the interfacial layer. Given the proposed 106 scenario, one needs to characterize the physicochemical properties of the interfacial layer in 107 these hydrogels so that the structure-property relationship can be established. This issue is 108 also important for other types of hydrogels with different interfacial coupling. In fact, 109 advanced characterization techniques have been utilized / developed to address this issue, 110 including the direct imaging and scattering spectroscopies, such as such as cryo-scanning electron microscopy (Cryo-SEM) and transmission electron microscopy (Cryo-TEM)^[24,25], as 111 well as Fourier infrared spectroscopy, Raman spectroscopy, and neutron scattering ^[26-28]. Here 112 113 it should be mentioned that the high density of CN-CN dipole pairs, AAm-AAm H-bonds, and 114 -SO₃H groups in PAN-based hydrogels are electrically polar. Given that hydrogels are mainly 115 utilized in environments of relatively slow requests, the low- and mediate-frequency dielectric 116 relaxation spectroscopy (DRS) could be a favored technique for probing the dynamic behavior of these polar units in the interfacial layer. 117



119

120 Figure 1. (A) A schematic drawing of the PAN-based hydrogel network structure, just for a 121 guide of eyes only. (B) A typical polymer structural unit with the well-crossed PAN-based 122 hydrogels, including the dual-physical interactions of dipole-dipole pairs and hydrogen bonds, 123 plus the covalent interaction.

124

125 In fact, DRS has been extensively utilized to characterize the electric responses of hydrogels, although the interfacial layer as a topic of DRS studies has been rarely touched ^[29-32]. This 126 127 situation is more or less due to intrinsic difficulty in the characterization itself and the 128 structural complexity of hydrogels. On one hand, a reliable separation of dielectric response 129 of the interfacial layer from those contributed from the two bulk phases seems to be an 130 insurmountable obstacle even though the interfacial layer's contribution is non-negligible. On 131 the other hand, high fraction of liquid water phase allows the polarizable water ions to 132 aggregate onto the electrode-hydrogel interface via rapid liquid diffusion (fast sufficiently to 133 respond to the low-frequency signals), generating the electrode polarization (EP) effect in the low-frequency range (e.g. f < 10 Hz)^[33]. Surely, this EP effect may not be quite large in the 134 135 relatively high-f range, but its magnitude is far sufficient to submerge all the intrinsic 136 dielectric signals which are also decreasing with increasing f. To overcome this barrier, the EP

137 effect in liquid water phase, must be suppressed as complete as possible. An immediate 138 approach is to replace real wet-hydrogel by ice-hydrogel in which liquid water is frozen into 139 ice phase so that the EP effect and other flowing-induced fluctuations can be avoided, since 140 no more inter-site diffusion can occur in the ice phase. Similarly, such inter-site diffusion 141 occurring inside the polymer phase would be largely suppressed if any. Differently, the local 142 fluctuations of polar molecules and electric dipoles remain less affected by replacement of liquid water with ice. Therefore, it comes to our attention that a DRS investigation on 143 144 ice-hydrogel may allow high opportunity to extract the dielectric relaxation in the interfacial 145 layer.

146

147 In this work, our major motivation is to utilize the DRS method to characterize the dielectric 148 response of those ice-hydrogels dominant with non-covalent bonding. Our major motivation 149 includes two points: one is whether the dielectric relaxation of the interfacial layer is 150 remarkable or not, and the other is the physicochemical properties of the interfacial layer 151 which is similar to or different from the bulk phase. The PAN-based hydrogels act as our 152 object of investigation mainly due to the fact that such hydrogels contain a relatively high 153 density of non-covalent bonds, and it will reveal that the interfacial dielectric response would 154 be remarkable in addition to the polymer bulk phase and water phase. It is thus suggested that 155 the interfacial layer may contribute largely to the physicochemical properties of the 156 PAN-based hydrogels, beneficial to understanding the mechanical and environment-sensitive 157 performances.

158

EXPEIMENTAL

160 Sample preparation

161 The PAN-based hydrogels were synthesized by the standard procedure ^[4]. The details of 162 synthesis were described in earlier reports and here only a brief description is given. A 163 schematic diagram for chemical reaction during the synthesis is drawn in Figure 2, following 164 the information given in Ref.^[4].



165

Figure 2. A schematic drawing of the molecular structure and the basic structure units of the 166 167 PAMPS for PAN-based hydrogel. Here stands the abbreviation of 168 Polyacrylamide-2-methyl-1-propanesulfonic acid, and PAN, PAAm, and PEGDA575 are 169 abbreviation of polyacrylonitrile, polyacrylamide, and polyethylene glycol diacrylate 170 respectively.

172 As an example for the synthesis process, 793 µl dimethyl sulfoxide (DMSO) was extracted by 173 pipette gun to centrifuge tub. Then 70 mg acrylamide (AAm) and 10 mg 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) were added into DMSO with 174 continuous stirring until complete co-dissolution of AAm and AMPS. Furthermore, 120 mg 175 acrylonitrile (AN) and 12.5 mg polyethylene glycol diacrylate (PEGDA575) were added into 176 177 the solution and stirred thoroughly. Finally, 6.4 mg 178 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (IRGACURE - 2959) as the 179 photo-initiator was added into the solution and stirred in nitrogen atmosphere until complete 180 dissolution. Subsequently, the mixture was poured into the mold. The ultraviolet light was 181 used to illuminate the mixture for one hour at room temperature, polymerizing it into hydrogel. The hydrogel was taken out from the mold and soaked in sufficient ultra-pure water. 182 In order to remove the non-reacted monomers and DMSO, the water had to be refreshed every 183

184 12 hour for 9 - 10 times, and the as-generated hydrogels were loaded in the beaker full of185 ultra-pure water in a state of readiness, for subsequent processing and experiments.

186

187 Microstructural characterizations

188 The water content in hydrogel samples is the first-priority parameter for structural 189 characterizations. Usually, the gravimetric method is used to measure the equilibrium water 190 content (EWC). In details, five pieces of regularly shaped hydrogel samples were fully 191 swollen in ultrapure water. Then the samples were taken out of the water container, removing 192 the surface water with wet filter paper for weighing on a balance. Then the samples were put 193 in the vacuum oven at 60 °C for drying until reaching a constant weight. The EWC parameter 194 is then calculated. In this work, we prefer to utilize the corresponding parameter f_w , the 195 equilibrium water content in volume percentage which seems to be more reasonable, defined 196 as:

197
$$f_{w} = \frac{m_{w} / \rho_{w}}{m_{w} / \rho_{w} + m_{p} / \rho_{p}},$$
 (1)

where m_w and m_p are the masses of water phase and polymeric phase in the wet-hydrogel, and $\rho_w \sim 0.92 \text{ g/cm}^3$ is the density of ice phase and $\rho_p = 1.0684 \text{ g/cm}^3$ is the density of dried-hydrogels (i.e. the polymer phase).

201

202 For characterizing the chemical bonding of the as-prepared samples, the Fourier transform 203 infrared spectroscopy (FTIR) of the hydrogels was measured using the NEXUS870 204 instrument manufactured by the NICOLET Company, USA. In more details, the 205 wet-hydrogels were put in the 75 °C vacuum oven to remove the water phase in very slow 206 sequence. Then the dried-hydrogels were put into mortar and ground into powder. The powder 207 was dispersed in potassium bromide, using a table press to press into a transparent sheet for FTIR measurement. The wave-number was from 4000 cm⁻¹ to 400 cm⁻¹ and the detection 208 accuracy was 2.0 cm⁻¹. 209

210

The microstructures at different scales were imaged by optical camera to shot the morphology of wet-hydrogels. The morphology of dried hydrogel as duplicate of the wet hydrogel sample

213 was imaged by means of environmental scanning electron microscopy (ESEM) using the 214 Quanta 200 instrument produced by the FEI Company, USA. To do this, the wet-hydrogels 215 were cut into regular rectangles for photographing. For the ESEM imaging, the hydrogels 216 were soaked in liquid nitrogen for one hour so that the original morphology of wet hydrogels 217 can be frozen. Subsequently, the frozen hydrogels were quickly transferred into the freeze 218 dryer that could continually work in -50 °C for 3 - 4 days. Finally, sprayed a thin gold film on 219 the cross section of the final hydrogel sample to prevent charge accumulation before 220 transferring into the ESEM sample stage for imaging.

221

222 The crystalline-like state of the as-prepared hydrogels was checked by means of the X-ray 223 diffraction (XRD) using the D8 Advanced instrument manufactured by the Bruker Company, 224 Germany. The PAN-based hydrogels in three different states were checked, including the dried-hydrogel, wet-hydrogel, and ice-hydrogel, in the θ - 2θ mode. These samples were 225 226 prepared as described below. The dried-hydrogels were obtained from the wet-hydrogels by 227 natural drying process at room temperature. The ice-hydrogels were obtained by inserting the 228 wet-hydrogels into the XRD sample stage whose temperature can be fixed between 200 K and 229 300 K using the liquid nitrogen cooling connection.

230

231 Besides, the differential scanning calorimetry (DSC) analysis on the as-prepared hydrogels 232 was performed using the DSC-200F3 instrument manufactured by the Netzsch-Geräebau 233 GmbH Company, Germany. Three samples with the same water content f_w were measured by 234 choosing the heating/cooling rates 5 K/min, 8 K/min, and 10 K/min respectively with 235 temperature T ranging from 240 K to 310 K. The storage moduli (G') and loss moduli (G'') of 236 the as-prepared wet hydrogels were tested using the TA Q800 dynamic mechanical analyzer 237 (DMA), produced by the TA Instruments Corporation, USA. The sample dimension was 15 238 mm in length, 6 mm in width, and 0.7 mm in thickness and measured in a submersion tensile 239 mode at 1 Hz in the warming sequence from 213 K to 310 K at 2.0 K/min.

240

241 Electrical measurements

The most important experiment for this work is the DRS measurement. The wet-hydrogels and pure ice plate were respectively cut the regular shape with 5.0 mm in length, 4.0 mm in width, and 1.0 mm in thickness and a capacitor-like geometry was used for the DRS probing. For the electrode preparation, the two pieces of gold foils of 5.0 mm \times 4.0 mm \times 0.1 mm in size were used as the top and bottom electrodes. Then the sample was frozen into the ice-hydrogel state and pure ice state for DRS probing.

248

249 Here, it should be mentioned that the ice phase would be gradually evaporated during the 250 DRS probing due to the cryo-based temperature control, if the measurement duration is long. 251 To avoid the evaporation, the hydrogel capacitor was sealed in a plastic bag to reduce 252 substantially the water evaporation in the cooling/warming sequences. The sample was in 253 good contact with the temperature control-stage and the cooling/warming rate remained 254 sufficiently slow (0.5 K/min or slower) to avoid possibly large difference in temperature 255 between the sample core and the sample hold-stage, noting that water/ice itself has relatively 256 good thermal conductivity. The HP 4294A impedance analyzer, manufactured by the Agilent 257 Company, USA, was used to carry out the DRS measurement in the frequency range of 40 Hz 258 to 1.0 MHz, and the ac-voltage signal is ~ 0.5 V in amplitude. It is noted that all the DRS 259 probing was run in the warming sequence starting from 200 K to 260 K. In this case, the 260 initial water-hydrogel sample sealed in the box was slowly cooled down to 200 K without any 261 electric bias in a rate of 0.5 K/min.

262

263 **RESULTS AND DISCUSSION**

264 Microstructures and chemical bonding

Before presenting detailed experimental results, a brief discussion on the structural units of the synthesized hydrogels schematically shown in Figure 2 is given, The polymeric network contain three major components that are respectively polyacrylonitrile (PAN), polyacrylamide (PAAm), and poly (2-acrylamide-2-methylpropanesulfonic acid) (PAMPS). In addition, a cross-linker polyethylene glycol diacrylate (PEGDA575) is copolymerized to form 3D network structure. This structure thus contains high-density non-covalently cross-linked units.

271	The dipole-dipole interaction in the PAN component and H-bond in PAAm component
272	constitute the dual physical-coupling mode with much lower chemical crosslinking density.

274 The as-prepared hydrogel sample in plate shape is visually shown in Figure 3A with water content $f_w \sim 0.78$. The color, transparency, and density are similar with earlier observations ^[4]. 275 276 The morphology and network structure for this sample after the drying treatment, imaged by 277 the ESEM, are presented in Figure 3B. The polymeric network channels of different sizes are 278 clearly imaged with typical channel diameter of several micrometers. This observation is well 279 consistent with the proposed pattern sketched in Figure 1A for wet-hydrogels, while the long 280 tube-like channels are more or less the consequence of network deformation during the water 281 evaporation and would not be discussed anymore.



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Figure 3. (A) The photo-image of the as-prepared wet-hydrogel sample ($f_w \sim 0.78$). (B) The ESEM image of the dry-hydrogel morphology. (C) The measured FTIR spectra for the wet-hydrogel sample. The XRD patterns of the wet-hydrogel, dry-hydrogel, and ice-hydrogel samples are plotted in (D), where the well-defined reflections from the ice-phase are labelled. (E) The measured DSC curves for this hydrogel sample, in the cooling-warming cycle with the cooling/warming rates of 5 K/min, 8 K/min, and 10 K/min respectively. (F) The measured storage moduli (G') and loss moduli (G'') as a function of temperature *T*.

291 For the chemical bonding, we look at the measured FTIR data on the wet-hydrogel sample at 292 room temperature, plotted in Figure 3C. Clearly, the stretching vibration mode at 1679 cm⁻¹ for C = O, symmetric and anti-symmetric stretching vibration modes at 3353 cm⁻¹ and 3207 293 cm^{-1} for – NH₂, both located with the PAAm unit, can be identified. The stretching vibration 294 mode at 1729 cm⁻¹ for C = O was from PEGDA575 crosslinker and the absorption peak of C 295 \equiv N at 2242 cm⁻¹ from the PAN unit can be identified too. Finally, the absorption peaks of O = 296 297 S = O at 1186cm⁻¹ and 1038 cm⁻¹ can be assigned to the PAMPS unit ^[34]. Therefore, the FTIR data indicate the co-existence of the PAN, PAAm, PAMPS, and crosslinker PEGDA575 298 units in our synthesized hydrogels, consistent with earlier report ^[4], and the non-covalent 299 300 bonding seems to be indeed the dominant one.

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302 The sample's crystallinity in different forms, as checked by XRD, can be discussed from the 303 θ -2 θ XRD spectra shown in Figure 3D. While the dry sample shows only weakly crystalline 304 or amorphous state of the polymer phase, indicated by the absence of any identifiable peak, the water hydrogel sample exhibits two broad bumps around $2\theta \sim 29^{\circ}$ and $2\theta \sim 43^{\circ}$, an 305 306 indicator of liquid phase nature. Here, it is noted that no remarkable characteristic peak from 307 the polymer can be seen, as a well-known fact. However, distinctly different from the two 308 samples, the ice phase in the ice-hydrogel sample is obviously of polycrystalline state with 309 well-developed crystal structure, evidenced by the existence of sharp peaks. The ice-hydrogel measured at 260 K exhibited main peaks at $2\theta \sim 22.6^\circ$, 24.3° and 26.2° , corresponding to the 310 (100), (002), and (101) reflections of hexagonal ice phase ^[35]. Meanwhile, there was a broad 311 but weak bump around $2\theta \sim 43^{\circ}$ that is likely from the amorphous state of the wet-polymer 312 phase. These characteristics show that the ice-hydrogels include the ice phase and 313 314 wet-polymer phase, while no clear indication from the interfacial layer can be seen from the 315 XRD data.

316

317 It should be mentioned that for the PAN-based hydrogels, earlier measurements on the 318 microstructure revealed the possibility for three-phase coexistence, including the good 319 crystalline phase, imperfect crystalline phase, and amorphous phase, respectively at $2\theta \sim 16.8^{\circ}$ 320 corresponding to the hexagonal unit of cyano groups, at $2\theta \sim 29.2^{\circ}$ and $2\theta \sim 38.6^{\circ}$ from the 321 amorphous water phase ^[36]. While the absence of any feature at $2\theta \sim 29.2^{\circ}$ and $2\theta \sim 38.6^{\circ}$ 322 indicates no glass or amorphous water phase, the absence of any sharp feature around $2\theta \sim$ 323 16.8 ° does confirm the amorphous polymer network. Therefore it can be argued that the 324 introduction of PAAm unit could deteriorate the possible crystallinity of polymeric phase 325 seriously, noting that the strong dipole-dipole interaction would favor the polymeric 326 crystallization ^[18].

327

While the polymer phase may not be well-crystallized, the presence of crystallized ice phase 328 329 in our samples can be further evidenced with the DSC data, even though the water phase is 330 separated by the polymer network into small-size droplets. The DSC data in the 331 cooling-warming cycle are plotted in Figure 3E with three different cooling/heating rates (5, 8, 332 and 10 K/min). While the ice-water melting sequences at the three rates show broad peaks 333 that are located roughly at the same position, the heat-release peaks during the solidification 334 are quite sharp with peak shifting toward the low-T side with increasing cooling rate, a typical 335 feature for crystal solidification process from liquid water. This demonstrates that the ice 336 phase is well crystallized in spite of polycrystalline nature due to the polymer network 337 confinement.

338

For further identifying the crystalline state of the sample, the DMA measurement was 339 340 performed too, by evaluating the elastic moduli (G') and loss moduli (G"). It is known that G' and G" are the two vital quantities to characterize the elasticity and viscosity of a material.^[37] 341 It exhibits the solid behavior if G' >> G'', while it is a liquid otherwise. In case of $G' \sim G''$, 342 one says that the material appears to be a semi-solid for example the hydrogel here. The data 343 344 of G' and G'' as functions of T are plotted in Figure 3F. It is seen clearly that the two quantities coincide with each other well roughly above 273 K, while one finds G' >> G'' in the 345 346 ice-hydrogel state confirming that the water phase is in well-crystalline state. Here, it should be reminded that the loss moduli G" at T < 273 K, the ice point of water, is non-negligible 347 348 even though G' >> G''. This effect is essentially related to the amorphous state of the 349 polymeric phase, contributing to the non-negligible loss moduli.

351 Remarkable interfacial layer contribution

After the characterizations on the microstructures of the PAN-based hydrogels, clear experimental evidence is now presented to reveal that the interfacial contribution is largely detectable in terms of the dielectric relaxation, and thus the interfacial coupling layer between the polymeric phase and water phase can't be ignored when the physicochemical properties are considered.

357

As a preparatory knowledge, we present in Figure 4A a crude schematic of the ice-hydrogel sample as inferred from the ESEM image of Figure 3B, where the ice grains and polymeric chain-networks constitute a two-phase interpenetrated composite. Given a hypothesis that the sample consists of water phase and polymer phase only, without the interfacial layer, it is well known that the dielectric constant ε_r (real part) of such a composite structure can be described by the famous Maxwell-Garnett equation ^[38]:

364
$$\varepsilon_r = \varepsilon_p \left(1 + \frac{df_w \beta}{1 - f_w \beta} \right), \quad \beta = \frac{\varepsilon_w - \varepsilon_p}{\varepsilon_w + (d - 1)\varepsilon_p}, \tag{2}$$

where ε_p and ε_w are the dielectric constants of the matrix (polymeric network) phase and filled particle (water/ice) phase, f_w is the water/ice content in volume fraction, and *d* is the spatial dimension of the hydrogel structure (*d* = 3).



Figure 4. The dielectric constant $\varepsilon_r(f)$ curves for all the samples measured at $T \sim 250$ K with 369 370 f-range from 100 Hz to 1.0 MHz. (A) A schematic of the ice-hydrogel structural model, where 371 the ice grains and polymeric chain-networks constitute a two-phase interpenetrated composite. 372 (B) The $\varepsilon_r(f)$ curves for pure ice and dried hydrogel. (C), (D), (E), and (F) The measured $\varepsilon_r(f)$ 373 data (open circle red dots) and evaluated $\varepsilon_r(f)$ data (open square black dots) from the 374 Maxwell-Garnett equation (Equation (2)) for a series of samples with $f_w = 0.245, 0.483, 0.589,$ 375 and 0.723 respectively, where symbol Δ indicates the difference between calculated and 376 measured $\varepsilon_r(f)$ data in the low-*f* range.

368

378 For DRS measurement, the frequency range covered is from 100 Hz to 1.0 MHz. The 379 dielectric constants for pure water/ice and dried PAN-based hydrogel (i.e. dry polymer 380 network) have been well measured, and one set of data at $T \sim 250$ K as an example are plotted in Figure 4B. It saturates at $\varepsilon_w \sim 60$ in the low-*f* range and $\varepsilon_w \sim 4.0$ in the high-*f* range, with 381 382 some frequency-dispersion in the intermediate-*f* range. The dried hydrogel shows much 383 weaker f-dependent dielectric constant and $\varepsilon_p(f) \sim 6.0$ in the whole f-range, consistent with 384 reported value. Given these data, one can estimate the $\varepsilon_r(f)$ data for the ice-hydrogels at 385 different f_w , as shown by the black open dots in Figure 4C-F for $f_w = 0.245$, 0.483, 0.589, and 386 0.723, where symbol Δ indicates the difference between calculated and measured $\varepsilon_r(f)$ data in 387 the low-f range, noting here again that no interfacial layer is included in the model 388 calculation.

389

390 Ideally, if the DRS signals can be simply viewed as the composite of ice phase and polymer 391 phase, the measured $\varepsilon_r(f)$ curves, the red curves, should be similar to the calculated ones from 392 Equation (2), the famous Maxwell-Garnett equation, i.e. the black dot curves. Surprisingly, 393 one finds the tremendous differences between them for all the samples of different f_w . Several 394 major features deserve for highlighting. First and most importantly, for all cases, the measured 395 $\varepsilon_r(f)$ is much larger than the calculated $\varepsilon_r(f)$. In particular, the low-f dielectric constant can be 396 two to three orders of magnitude larger than the predicted value. Noting that the EP effect 397 dominant in wet-hydrogels is almost avoided here, this big difference must be ascribed to the 398 contribution from the dielectric relaxation in the interfacial layer where high-density of polar 399 molecules or dipole units may be available. Second, for the f_w -dependence, it is seen that the 400 low-f dielectric constant increases with increasing f_w until $f_w \sim 0.8$, beyond which the 401 measured $\varepsilon_r(f)$ falls down towards the value of dried hydrogel.

402

The data presented in Figure 4 demonstrate with no doubt that the interfacial layer can be one of the major components for contributing to the dielectric relaxation of the whole hydrogel structure and likely other functionalities, according to the DRS data presented here. This issue has less been addressed earlier, mainly owing to the fact that the earlier DRS investigations 407 were mainly performed on wet-hydrogels instead of ice-hydrogels here. In such case, the EP 408 effect is somehow significant and the interfacial contribution is basically submerged. In the 409 other words, the large difference Δ may be improperly treated as the contributions of the EP 410 effect. Here the case is different and the PAN-based ice-hydrogels are measured without much 411 influence from the EP effect.

412

413 **Overall dielectric relaxation**

414 The DRS measurements on a series of ice-hydrogels at different f_w were performed and the 415 data were thoroughly checked. It is not our intention in this work to discuss in details the 416 difference in the DRS data among these samples of different f_w . Instead, the common 417 dielectric relaxation characters of these ice-hydrogels that can reflect the interfacial layer properties will be described. As an example, the measured DRS data for sample $f_w = 0.483$ in 418 419 the ice-hydrogel state, are shown in Figure 5A and B for the collected $\varepsilon_r(T)$ and dielectric loss 420 $tan\delta(T)$ at a set of frequency f, measured in the warming sequence from low-T side to 260 K 421 beyond which the ice begins to melt.





Figure 5. (A) and (B) Measured dielectric real part ε_r and loss tan δ at several frequencies as a function of *T* for the as-prepared wet sample ($f_w = 0.483$) in the warming sequence from 200 K. For a clearer illustration, the measured $\varepsilon_r(T)$ and tan $\delta(T)$ data at f = 10 kHz are presented in (C). (D) Evaluated T_{max} .vs. *f* relationship from which the thermal activation energy E_a is evaluated via the Arrhenius law.

429 At first glance, it is clear that dielectric relaxation spectrum evidences the behavior of bulk ice 430 phase with strong frequency-dispersion. For a given frequency f, the dielectric real part $\varepsilon_r(T)$ 431 increases with increasing T and this increasing tendency is strong in the low-f range and 432 becomes much weaker in the high-f range, as shown in Figure 5A. On the other hand, the 433 dielectric loss part $tan\delta(T)$ for all frequencies demonstrates clearly the wide- and single-peaked dependence of T with the peak location at T_{max} , as shown in Figure 5B. The 434 435 dielectric frequency-dispersion is also evidenced by the remarkable shifting of the loss peak 436 with increasing *f*.

437

For a clearer presentation of these relaxation features, the $\varepsilon_r(T)$ and $\tan\delta(T)$ data measured at f= 10 kHz are plotted in Figure 5C in the linear coordinate plane. The sharply increased $\varepsilon_r(T)$ and the broad peaked $\tan\delta(T)$ at T_{max} are more clearly presented. By extracting the values of T_{max} at a series of f, one obtains the (T_{max}, f) dataset and plots them in Figure 5D in the $\ln f \sim$ T^1 plane. One observes the linear $\ln f \sim T^1$ dependence. This dependence can be more or less described by the well-known Arrhenius law ^[39]:

444
$$f = f_0 \cdot \exp(-E_a / k_B T_{\text{max}}), \tag{3}$$

where f_0 is the frequency-prefactor, k_B the Boltzmann constant, and E_a the thermal-activation energy for the dielectric relaxation while its clear indication needs more discussion. The best fitting of the data gives $E_a \sim 53.46$ kJ/mol, the thermal-activation energy for the dielectric relaxation.

449

450 Thermal-activation energy and discussion

Given the above analysis, one is now able to discuss the influence of parameter f_w , the water content on the physicochemical properties of the ice-hydrogels. The measured $\varepsilon_r(T)$ and tan $\delta(T)$ data at four different f_w are plotted in Figure 6A and B respectively. Beside the rapid increasing with increasing *T*, the measured $\varepsilon_r(T)$ becomes larger at higher f_w , in particular in the *T*-range close to the melting point of ice. What should be concerned here is the measured tan $\delta(T)$ curves at these different f_w . Each curve exhibits remarkable and broad peak and the peak location T_{max} shifts remarkably, reflecting the strong role played by the interfacial layer. 458 Here, two issues should be mentioned. First, the measured loss in the *T*-range is quite large, 459 and reaches $\tan \delta \sim 1.0 - 3.0$ even at low water content ($f_w = 0.245$), noting that pure 460 PAN-based polymer phase is of very low tan δ in this *T*-range and the typical value is 0.02 ~ 461 0.03. Therefore, the loss most likely comes from the interfacial layer, noting the bulk ice 462 phase is well-crystallized and the d.c. electrical conduction of the samples is very low 463 (excluding the potential contribution from the *d.c.* conduction to the loss). Second, the strong 464 peak shifting at different f_w also suggests the remarkable contribution from the interfacial 465 layer. Otherwise, the loss peak would remain non-shifting although the loss intensity would increase with increasing f_w , if the loss signals would majorly come from the bulk ice phase. 466





Figure 6. The measured $\varepsilon_r(T)$ and $\tan\delta(T)$ data at four different f_w are plotted in (a) and (b). (c) The evaluated E_a of the ice-hydrogel samples as a function of f_w .

To this stage, it has been revealed that the dielectric responses of the PAN-based hydrogels include the remarkable contribution from the interfacial layer, and this is the first time to address this issue and reveal this fact. This interfacial layer contribution would be expected to reach the maximal roughly at $f_w \sim 0.5$, given the two-phase model scenario where the interfacial layer would occupy the highest volume fraction. Indeed, it can be seen from Figure 6B that the peak is the highest for $f_w \sim 0.589$ and becomes lower again when f_w is roughly larger or smaller, e.g. the cases for $f_w = 0.389$ and 0.723 where the peak intensity and T_{max} (as indicated by arrow) are lower than those for $f_w = 0.589$.

478

479 Finally, the thermal-activation energy E_a of the ice-hydrogel samples as a function of f_w , 480 should be discussed qualitatively, and the evaluated values simply from the Arrhenius law are 481 shown in Figure 6C. It is clearly seen that the activation energy is roughly constant, i.e. $50 \sim$ 482 60 kJ/mol, roughly independent of the water content, a reasonable outcome assuming the 483 whole set of samples have similar interfacial coupling properties. Furthermore, the value of pure ice phase, E_{aw} , is also ~ 58 kJ/mol ^[40,41]. The similar activation energy values between 484 the ice-hydrogels and pure ice sample suggest the similar dynamics of the electric dipoles 485 486 (molecules, dipoles, and other bonded units) in the interfacial layer to those polar water 487 molecules. Considering the major non-covalent bond structure in the interfacial layer, this 488 result is physically reasonable. Instead, one can expect that the much larger activation energy 489 for those hydrogels with strong covalent bonding between the polymer phase and water.

490

491 CONCLUSION

492 In summary, the PAN-based ice-hydrogels dominant with non-covalently bonded structure have been investigated by performing a series of microstructural, thermo-mechanical, and 493 494 chemical bonding characterizations. In particular, the dielectric relaxation spectroscopy (DRS) 495 of the ice-hydrogel samples with different water/ice content f_w was measured, in order to 496 avoid the serious EP effect available in the water-hydrogel state. This DRS measurement on 497 the ice-hydrogels allows a comprehensive investigation of the polymer-water interfacial 498 layers and their roles in determining the physicochemical properties of the hydrogels. It is 499 revealed that this set of PAN-based hydrogels exhibit remarkable contribution from the 500 polymer-water interfacial layers in terms of dielectric relaxation, an effect that has less been 501 addressed. The dielectric response of the hydrogel samples is largely from the interfacial 502 layers rather than the polymer network phase and ice phase, at least in the low frequency 503 range. The present work demonstrates the substantial roles of the so far less-addressed

504	polymer-water interfaces, and would sheds essential light on our understanding of the			
505	structure-property relationship in hydrogels.			
506				
507	DECLARATIONS			
508	Authors' contributions			
509	Made substantial contributions to conception: J. M. Liu			
510	Design of the study: Y. Q. Li, Z. B. Yan, and J. M. Liu			
511	Data analysis and interpretation: Y. Q. Li and Z. B. Yan			
512	Data acquisition: Y. Q. Li and W. J. Zhai			
513	Administrative, technical, and material support: W. G. Liu, B. Liu, C. F. Li, L. Lin,			
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515	Manuscript writing: J. M. Liu, Z. B. Yan, and Y. Q. Li			
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